Detonation Products Equation of State

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Most high explosives in common use have a chemical formula of the form $C_aH_bN_cO_d$, where a, b, c, and d are integers. Upon detonation, the products are composed of a molecular fluid mixture of N_2, CO_2, H_2O, some CO, and other minor molecular species. In addition, solid carbon clusters are produced in predominately graphite or diamond phases with surface restructuring and/or surface groups capping dangling bonds. Typical conditions are pressure around 30 GPa, temperature 3000 K, and density 2.4 g/cm³.

We are using a wide variety of methods to characterize detonation products equation of state (EOS). The EOS schemes range from empirical forms fit to a large data set, to thermodynamic perturbation theory, to a Composite Monte Carlo method [1, 2, 3] giving chemical equilibrium composition including the dense fluid mixture and solid carbon clusters. This presentation will focus on an *ab initio* method that looks like it could predict an accurate detonation products EOS.

High density fluid nitrogen has been chosen as the first test case for this method. Subsequent studies will involve other major detonation product species and their mixtures, with the final goal being an accurate predictive EOS for typical high explosives. The *ab initio* studies will either be used directly or as a benchmark to calibrate other methods.

There are two major aspects of a high density fluid EOS, an accurate evaluation of the energy of important configurations and a thermodynamic sampling of the chosen configurations.

Configurational energies are determined using the MondoSCF [4] code which gives very efficient (linear scaling) many-particle *ab initio* electronic structure calculations. With configurations of around 100 molecules and periodic boundary conditions, the focus is on the accurate evaluation of the many-body energy in those configurations. An extensive study of basis set dependence for individual molecules, pairs of molecules, and full many-body configurations was conducted along with an evaluation of the accuracy of various density functional methods.

At high density, a significant many-body contribution was found. The PBE0 density functional was found to give a good representation of the nitrogen energy and bond length. A 6-31G** basis set was found to give convergent results for the difference in energy between fluid configurations and isolated N_2 molecules (using ghost basis functions). Even with the high efficiency of MondoSCF, a single configuration requires a substantial amount of computer time (~2 days on a single processor).

The standard Monte Carlo and molecular dynamics methods require a very large number of configurations for evaluation of the thermodynamics. In order to control the number of configurations required, we have developed a method that gives qualitative results with 10 configurations and accurate statistics with 100. First, a reference simulation is made in the NPT ensemble with a reference pair potential that is very close to the many-body interaction. In this case, a fit to the calculated two-body anisotropic interaction was used. Then the full many-body electronic structure energy was evaluated using MondoSCF for uncorrelated sample configurations from the reference sample. Instead of relying on a perturbation expansion, each sample configuration was reweighted for the full energy thermodynamic distribution. In principle, this is exact, but in practice the reference distribution is peaked in the wrong location for the full sample. By choosing the P and T of the full simulation to be different from that of the reference simulation, the peaks of the two distributions can be adjusted to have maximum overlap and good statistics after all.

For the nitrogen fluid, a large set of EOS points has been calculated over the range of around 5–40 GPa. Temperatures are chosen to be near those of the Hugoniot. Using the shock jump conditions, a theoretical
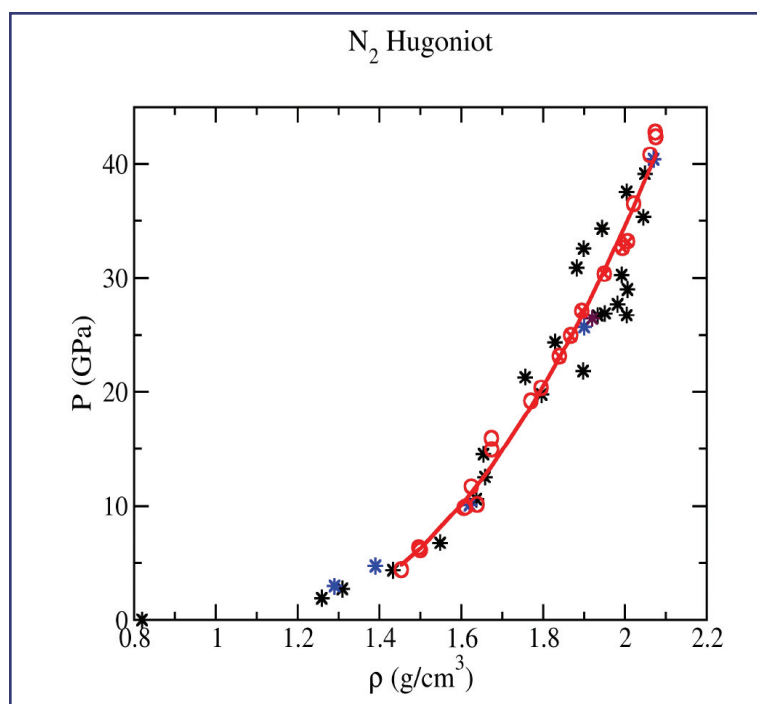
N_2 Hugoniot

Hugoniot has been calculated. The results are in excellent agreement with experiment and look to be predictive. In Fig. 1, the Hugoniot data are given with the $*$ symbols. Calculated results are given in red. The open circles are from samples with 10–20 configurations per EOS point. The X is included in the circle to denote samples with 30–50 configurations and correspondingly smaller statistical uncertainty. Additional configurations are being calculated to improve the statistics. The red line is a fit to the set of calculations.

The many-body results are in excellent agreement with experiment. (Previous calculations with an *ab initio* pair potential are roughly 20% higher in pressure.) The next step will be to calculate CO_2, H_2O, and CO fluids. Then combinations of these will be evaluated in mixtures. The results for high explosives products are very sensitive to the details of the interactions of unlike molecules because of resulting shifts in chemical equilibrium. These calculations along with limited experimental data can be used to make significant improvements in the precision and predictability of EOS models.

[1] M. Sam Shaw, "Direct Simulation of Detonation Products Equation of State by a Composite Monte Carlo Method," (to be published in *Proceedings of the 12th Detonation Symposium*).
[2] M. Sam Shaw, "A Hybrid Monte Carlo Method for Equilibrium Equation of State of Detonation Products," in *Shock Compression of Condensed Matter - 2001*, edited by M.D. Furnish, N.N. Thandhani, and Y. Horie (AIP, 2002), p. 157.
[3] M. Sam Shaw, "Direct Simulation of Detonation Products Equation of State," (to be published in *Proceedings of the 2003 APS Topical Conference on Shock Compression of Condensed Matter*).
[4] Matt Challacombe, et al., "MondoSCF, A Program Suite for Massively Parallel, Linear Scaling SCF Theory and *ab initio* Molecular Dynamics," Los Alamos National Laboratory computer code LA-CC 01-2.

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